PREPARATION AND PROPERTIES OF HYDROPHILIC PLASMA POLYMER FILMS

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Abstract

Plasma polymers of Ar/n-hexane/water have been deposited on surfaces of a plasma polymer from Ar/n-hexane predeposited on glass. Wettability of latter "model" polymeric material was thus modified. It has been found that wettability improves with an increase of water vapour concentration in working gas mixture or with increased power to the discharge. FTIR data indicate an increase of contents of polar groups with time in the films stored in humid environment.

Introduction

Modification of surfaces of solids by changing their wettability has been performed in a number of ways. For example low pressure oxygen (air or steam) plasma treatment enriches a polymer surface by polar groups thus enhancing wettability. However polar groups are slowly buried inside the polymer as it has been explained by Yasuda et.al. [1]. They suggested in more recent work [2] at first to deposit a plasma polymer of CH_4 and then apply oxygen or wett air plasma treatment. Because the plasma polymer was highly crosslinked the overturn of polar groups has not been so easy so that time duration of wettability has been improved.

Deposition of a wettable plasma polymer on the treated surface has been investigated by number of researchers using as monomers the both unsaturated [3] and saturated alcohols, amines and amides [4,5], ethylene/ O_2 [6] or acetone/ O_2 [7]. Some groups mixed water vapour with their monomers for plasma polymerization [3,8].

In this work a simple parallel plate electrode (mesh cathode) system for dc glow discharge for plasma polymerizaton of Ar/ n-hexane/ H_2O mixture has been used. Results of this study are described below.

Experimental

The deposition arrangement is shown in Fig. 1. A grid cathode of 4x 5 cm made from stainless steel wire was inside the anode (earthed) with spacing of 2 cm on the both sides. (See Fig.1.) The quartz crystal microbalance was used to monitor deposition rate. Glass substrates rested on the caroussel holder being a part of the anode. This electrode system was placed in the barrel of a diffusion pumped stainless steel chamber. Calibrated needle valves feeded Ar, water and n-hexane vapours, respectively into the chamber. In each experiment background pressure (10^{-3}Pa) was kept for one hour and then the flow rate of n-hexane was fixed constant. Desirable pressure measured by MKS Baratron gauge was established by throttling the diffusion pump. Then water vapour and argon were added to required pressures and dc discharge ignated. Up to 6 substrates without breaking vacuum were deposited. As substrates a soda lime silicate glass (blank and predeposited by Ar/n-hexane plasma polymer) was used.

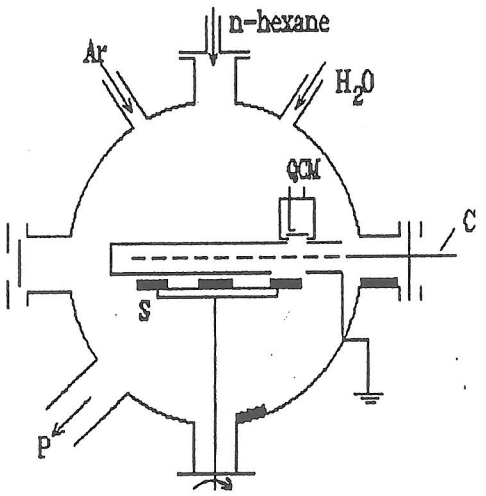

Fig.1 Deposition arrangement : S- substrate, C- catode, QCM - quartz crystal microbalance monitor, P- to pumps, Ar, n-hexane, H_2O - inlets.

Wettability of the treated model polymeric surface (a plasma polymer of n-hexane) was assessed by a bouble

method using distilled water at a room temperature on self built equipment.

FTIR absorption spectra were measured on films deposited on Si substrates using NICOLET Impact 400 Spectrometer. More details on the experimental precedures can be found in Refs. 9, 10.

Results and Discussion.

For wettability study we predeposited glass substrates with a plasma polymer of n-hexane/ Ar mixture of a thickness 100 nm. "Plasma modification" of this model polymer surface was performed by depositing a plasma polymer using Ar/n-hexane/water mixture. The example of the mentioned wettability modification is in Fig. 2 that shows the decrease of contact angle with the increase of water vapor contents in the mixture. Hysteresis is observed between the receeding and advancing angles that come close each other as the H_2O contents increases.

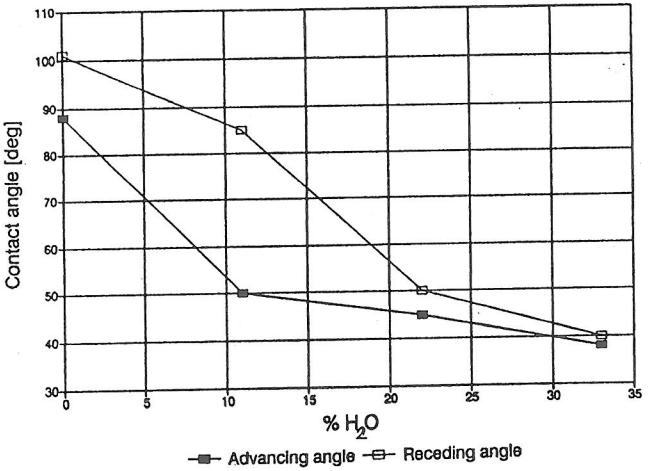

Fig.2 Contact angles in dependence on water contents in the gas mixture Ar/n-hexane/water

We used for deposition working gas mixture at total pressure ranging from 13 Pa to 39 Pa always of the same ratio of components approximately 60% of Ar and 40% of n-hexane + water. An example is given in Fig. 2 for total pressure p_t = 36 Pa (p_{Ar}= 24 Pa, $p_{water + n\text{-}Hexane}$= 12 Pa). The deposition rate related to unit power decreases from 0,01 nm/Ws with increasing water contents in the mixture. The ablation of treated polymer surface starts beyond 30-35% of H_2O.

Earlier we observed a decrease of contact angle values with increased power for sample deposition when as monomers alcohols were used [11]. Similar behaviour we found also in the present case - see Fig. 3. Formerly it was also mentioned for plasma polymerized hexamethyl disiloxane [12].

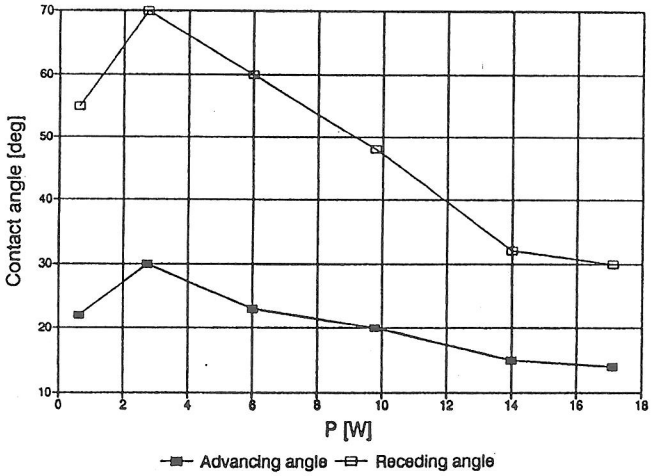

Fig.3 Contact angle versus power P (deposition parameters: p_t= 36Pa, gas mixture: Ar + H_2O + n-hexane: 67% + 28% + 5%).

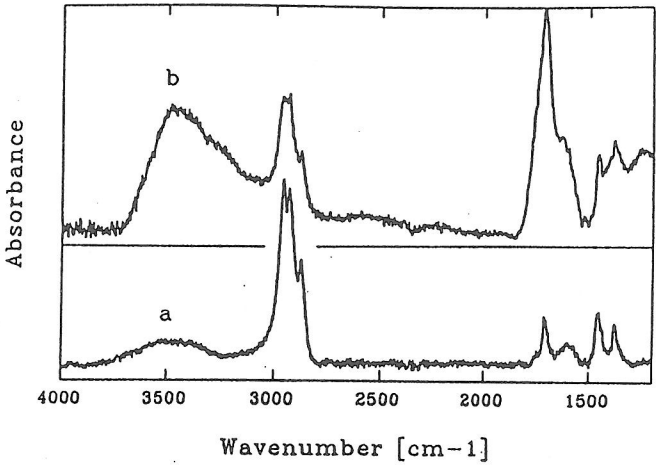

Fig.4 FTIR absorption spectra of sample prepared at the following conditions:discharge parameters 700 V/ 14mA, p_t= 36 Pa, gas mixture: Ar+ n=hexane+ water (67%+ 1%+ 32%). Curve a- immediately after deposition, curve b- after 150 days.

FTIR absorption has been measured for films deposited on Si - an example is in Fig. 4. The main absorption bands are caused by stretching in groups:

OH in spectral region	3500 cm^{-1},
CH	2900 cm^{-1},
C=O	1700 cm^{-1}.

Spectra reflect the increased contents of water in a working gas mixture during the preparation of respective samples [10]. It can be concluded that also in our case of wettable plasma polymer its functional character is based on hydroxyl/ carbonyl. The band near 1600 cm^{-1} can be assigned to some specific sites of C=O groups conjugated with hydrogen-bond or OH group.

We have examined long term (150 days) development of FTIR absorption spectra. (Please see Fig.4.) Very similar changes of diffusion reflection spectra of a powder poly (dimethylfulvene) measured during oxidation in air were observed by Fuller and Griffiths [13]. In Fig. 5 time change of various relative absorption peak intensities is shown. Time dependence $CH_x(t)$ near 2900 cm^{-1} is plotted relative to its initial value $CH_x(0)$. OH near 3500 cm^{-1} and CO near 1700 cm^{-1} are given relative to the $CH_x(t)$ in the same spectrum. The biggest alteration happened during 30 days period when the sample was stored at room temperature in saturated vapour pressure of water. Possible explanation of the change of the FTIR spectra after 150 days may be the cracking and seggregation of the film parts according to their hydrophilicity. Area of the overall surface (including surfaces on cracs) increases and therefore the incorporation of OH and C=O is much easier.

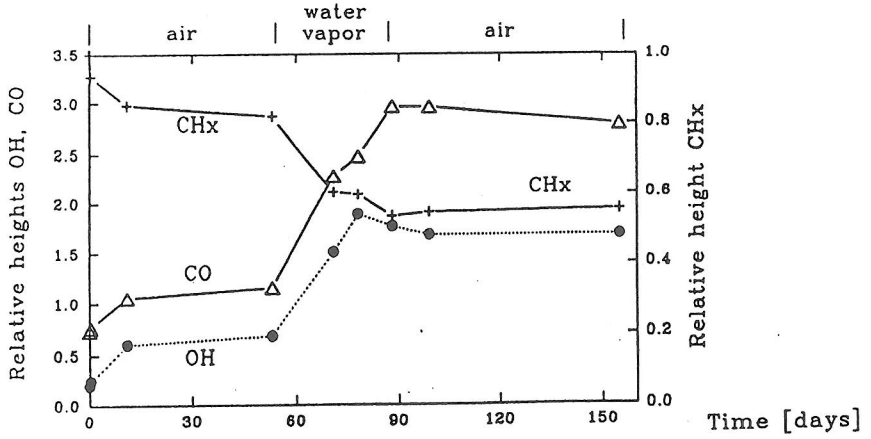

Fig.5 Time development of FTIR absorption relative peak intensity for the same sample as in Fig. 4.

Conclusions

Wettability of a polymeric surface is raised with the increase of water vapor contents in a working gas mixture.However the increased presence of water vapour decreases the deposition rate. Wettability of films also improves if the power used for depposition is enhanced. According to FTIR measurements the presence of polar groups OH and C=O increases when the sample is stored in humid environment.

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